Studying the Thermal Effect and Nano Zinc Oxide Load Level on the Adhesion Between Rubber Compound and Steel Tire Cords

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Abstract

In this research, T-adhesion of samples were evaluated at (25,50,75 and 100) °C temperature. The effect of nano-zinc oxide loading on rubber-tire cords interface is investigated by replacing of conventional zinc oxide by nano-zinc oxide as an activator. One compound has conventional zinc oxide as an activator with 8pphr (part per hundred rubber). Eight compounds have nano-zinc oxide with (0.2, 0.6, 1, 1.4, 1.8, 2.2, 2.6 and 4) pphr so as to improve adhesion force and reduce the amount of zinc oxide inside the compounds.

The results show that the increasing temperature leads to decrease the adhesion in the rubber-tire cords interface. The maximum value of adhesion force with nano-zinc oxide is occurred at 2.2 pphr. The replacement of conventional zinc oxide by nano-zinc oxide leads to improve the pull-out force by 12%. Also, it reduces the amount of zinc oxide by 72.5%. Furthermore, it leads to reduce the cost of compounds. Finally, it reduces the negative effect of zinc oxide on the environment by reduction in the amount of zinc oxide inside the compounds.

Key Words: T-adhesion, Conventional Zinc Oxide, Nano-Zinc Oxide and Steel Tire Cord.

الخلاصة

في هذا البحث، عينات التلاصق T تحسب عند °C(100,75, 50, 25) . درس تأثير تحميل أوكسيد الزنك النانوي على سطح اسلاك الإطار مع المطاط بتبديل أوكسيد الزنك الاعتيادي باوكسيد الزنك النانوي كمنشط. احدى العجنات تحتوي على أوكسيد الزنك الاعتيادي كمنشط بتركيز8pphr (جزء من مائة من وزن المطاط) . ثمان عجنات تحتوي أوكسيد الزنك النانوي بتركيز(4, 2.75, 2.2, 1.8, 1.4, 1, 0.6, 0.2pphr) لزيادة قوة التلاصق وتقليل كمية أوكسيد الزنك داخل العجنات.

بينت النتائج ان زيادة درجة الحرارة تؤدي الى نقصان التلاصق عند سطح اسلاك الإطار مع المطاط. أعظم قيمة لقوة التلاصق عند 2.2pphr أوكسيد زنك نانوي. استبدال أوكسيد الزنك الاعتيادي باوكسيد الزنك النانوي يؤدي الى تحسين قوة السحب ب 12%. كذلك تقلل من أوكسيد الزنك ب 72.5%. بالإضافة الى ذلك تؤدي الى تقليل الكلفة للعجنات. اخيرا يقلل من التأثير السلبي لأوكسيد الزنك على البيئة وذلك بتقليل كمية أوكسيد الزنك داخل العجنات.

الكلمات المفتاحية :- عينات التلاصق T، اوكسيد الزنك الاعتيادي ، اوكسيد الزنك النانوي ، اسلاك الاطار الفولاذية.

1. Introduction

Rubber is generally called elastomers. They are used in many engineering applications due to their low cost, wide availability, dissipating energy, resiliency, long service life, light weight and it can be simply molded into any shape. Applications of rubber are presently used in coatings, cables, medical/dental, tires, optical devices, engine mounts and gaskets (Hadi *et. al*., 2015)

Major improvements in tire quality have been achieved with the production of composite structure of rubber and metallic wires. The product depends on the strength of the adhesion between rubber and wire. Natural rubber compounds don't directly adhere to steel metal. Therefore, the usage of a thin brass coating of twisted steel cords is very important to prevent rusting(**Harakuni,2007)**.

Steel cord coated with a thin layer of brass is drawn during the forming process. The zinc ions (Zn^{2+}) diffuse to the surface and are oxidized to a zinc oxide (ZnO) layer and a very small amounts of copper oxide (CuO) film is created. Through vulcanization (curing),active sulphur in rubber compound touches the copper in the brass coat and a strong copper sulfide (CuS) bonds are shaped during sulphidation between the cords and the rubber compound **(Crowther, 2003)**. Copper sulfide domains are formed on the surface of the brass film during the vulcanization reaction. These domains have a high specific surface area and are produced within the wire coat compound before the polymer is cross-linked into an elastomeric network **(Erman *et.al.*, 2013 ;Rodgers, 2004)**.

Degradation of the wire-rubber adhesive bond is catalyzed by Zn^{2+} ions, which diffuses through the interfacial CuS flim. It leads to an excess of either ZnS or ZnO. The Zn^{2+} ions will travel to the surface, with following drop in the mechanical interlocking of the CuS domains and rubber subsequent by degradation of adhesion. The mechanism of this process is illustrated in Figure 1.

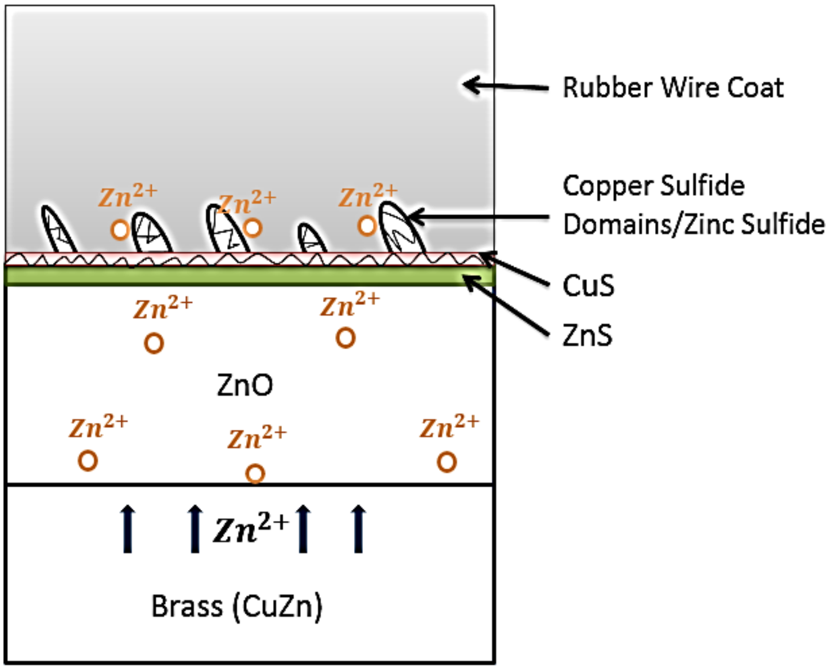

Figure 1: Mechanism of Rubber-Brass Bonding.

To reduce Zn^{2+} ions, it is suggested to replace the conventional ZnO by nano-ZnO, which has a very small particle size (10-100 nm). The surface area of the nano-ZnO is higher than that of conventional ZnO (**Heideman *et.al.*, 2004)**. Low level loading from nano-ZnO improves physical properties in comparing with the same level of the conventional ZnO.

Due to temperature increase through running tire, the energy of adhesion will differ as compared with the initial state. To study the adhesion force between rubber compound and steel tire cord at raised temperatures, the T-pull test method was used. T-pull test is a simple method for adhesion evaluation at ambient temperature.(**Hiedman *et.al.*, 2004)**investigated the effect of conventional ZnO and nano-ZnO with particle size (20-40 nm) on rubbers. They found that only one-tenth of the amount of nano-ZnO in comparison with the conventional ZnO was necessary to achieve the same cure characteristics. Also they, found that replacement of conventional ZnO by nano-ZnO led to an improvement of the properties of the rubber compound, especially the abrasion resistance, H pull-out force and tear strength. (**Jamshidi *et.al.*, 2005)** studied the effect of elevated temperatures on cord-rubber interface adhesion which were (25, 50, 75, 100, 125 and 170) °C at vulcanized temperatures (130,140, 150 and 160) °C. They found that in all cases, an increased in temperature causes a decrease in adhesion force and that best vulcanized temperature is at 150 °C.

The main objective of the present research is to investigate the effect of temperature and nano-ZnO load level on the adhesion force of the natural rubber compounds used in Babylon tires factory in Iraq. The test results will be a key factor in determining the best compound choice for the tire industry.

2. Experimental Work

2.1 The Used Materials

The materials used in the experiments are Natural rubber (SMR20), Conventional Zinc Oxide (purity=99%, Particle size=0.5-1µm, and surface area=3-5m^2/gm.), Nano Zinc Oxide (Purity=99% and Particle size<80nm), phthalimide (CTP-100), stearic acid, phenolic tack resin, anti-ozinants (6PPD), carbon black, process oil, cobalt stearate, accelerator (DCBS), sulfur and steel wire construction (2+2*0.28 mm) coated with brass (Cu/Zn, 64/36) %.

2.2 Preparation Technique

The formulation of the rubber compounds is illustrated in Table 1. (A) group involves the standard compound used in Babylon tires factory including 8phr conventional ZnO. (B) group includes the compounds Nano-ZnO with the same concentration of other materials in (A) compound. Compounds were prepared by two-roll laboratory mill (300×150) mm as shown in Figure 2. The ingredients were added as follows:

1. The SMR20 was masticated in two roll mills several times with decreasing the distance between the rolls at a constant temperature at 70◦C.
2. The ZnO is added to the SMR20 and the same procedure in step (1) was repeated.
3. The following additives are added to the mixture of SMR20 and ZnO in sequence. They are stearic acid, 6PPD, cobalt stearate and phenol tack resin and the same procedure in step (1) was followed.
4. A half of carbon black (25 pphr) was mixed with oil then it was added to the homogeneous materials by following the same procedure in step (1).
5. Adding the other half of carbon black was added alone and finally sulfur, CBS and CTP-100 were added and the same procedure in step (1) is followed.

It is important to mention that the total mixing time is kept to be minimum in order to avoid sticking of the rubber compound to the mill rolls. Table 2 shows the time for all processes according ASTM D15.

Table 1: Compounding Recipes of The Mixes in pphr.

Material	A	B1	B2	B3	B4	B5	B6	B7	B8
SMR20	100	100	100	100	100	100	100	100	100
ZnO	8	-	-	-	-	-	-	-	-
Nano-ZnO	-	0.2	0.6	1	1.4	1.8	2.2	2.75	4
Stearic acid	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
6PPD	1	1	1	1	1	1	1	1	1
Phenol tack resin	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Carbone Blake	50	50	50	50	50	50	50	50	50
Oil Process	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7
Cobalt stearate	1	1	1	1	1	1	1	1	1
DCBS	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Sulfur	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
CTP-100	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4

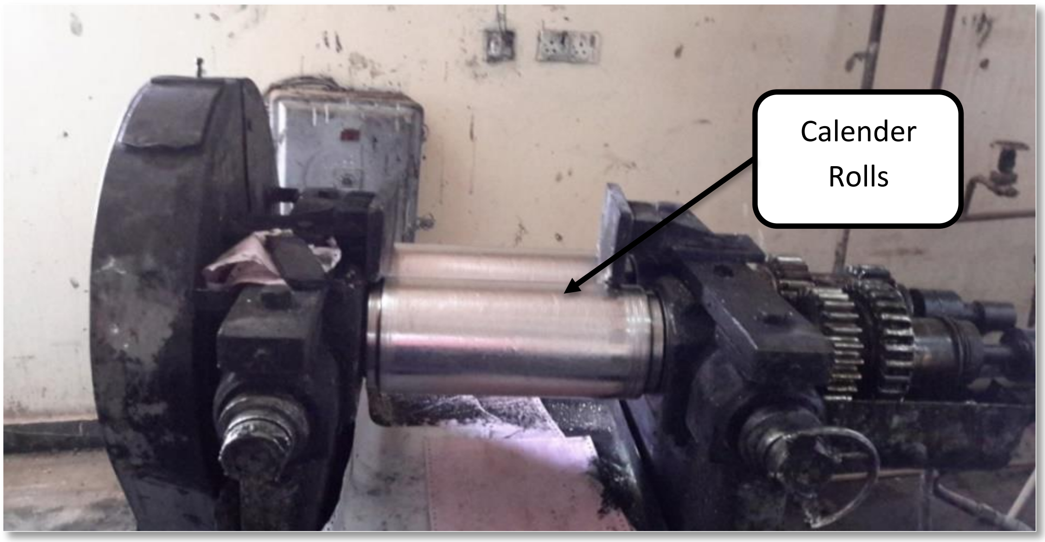

Figure 2: The Calendering Machine.

Table 2: Mixing Schedule.

NO	Operations	Time (minutes)
1	Mastication of SMR20 rubber	4
2	Addition of zinc oxide	2
3	Stearic acid, 6PPD, cobalt stearate, phenol tack resin	2
4	Addition of carbon black + oil	6
5	Addition of carbon black	4
6	Sulfur, CBS, CTP-100	4
7	Sweep and dumb	3
8	Total	25

2.3 Vulcanization Process

The rubber in original state is generally not very strong. It doesn't maintain its shape after a large deformation, having its consistency as gum. It cannot be made without vulcanization or curing. Vulcanization is a process usually applied to rubbery or elastomeric materials. It can be defined as a process which increases the retractile force and reduces the amount of permanent deformation residual after removing the deforming force. Thus, vulcanization decreases plasticity while it increases elasticity **(Erman *et.al.*, 2013)**.

The vulcanization process of the previously mentioned rubber compound is started by heating the hydraulic press which is used in the vulcanization process as it is shown in Figure 3. It consists of two jaws used to generate high pressure on the mold which has three parts:- base die, cover die which have similar in dimensions (300×150×5) mm, and steel die with dimension (300×115×12.5) mm. The last one has a hole with dimension (200×12.5×12.5) mm for inserting the specimen inside the hole and has 15 grooves for inserting the steel wire inside grooves, Figure 4.

To produce a T-adhesion specimen, the unvulcanized piece was cut into two parts with the same dimensions and inserted into the hole, wires were put in grooves to embed into the piece then another piece was put on the first and the press is closed in the possible minimum time. When the piston reached 145°C, the mold put between jaws and pressed at 3.5 MPa for 30 min according to ASTM D3182. To obtain a specimen of adhesion test, they must be cleaned after vulcanization as it is shown in Figure 5.

Figure 3: Thermal Hydraulic Press.

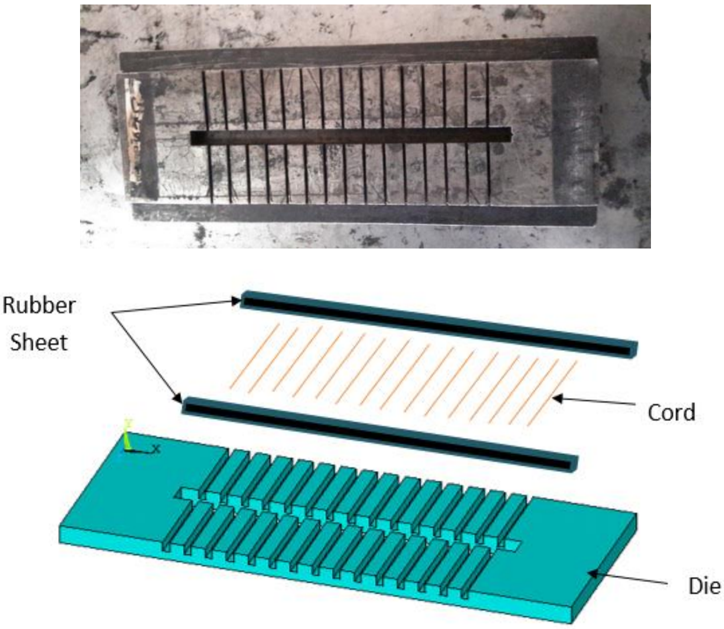

Figure 4: Mold of Adhesion Sample.

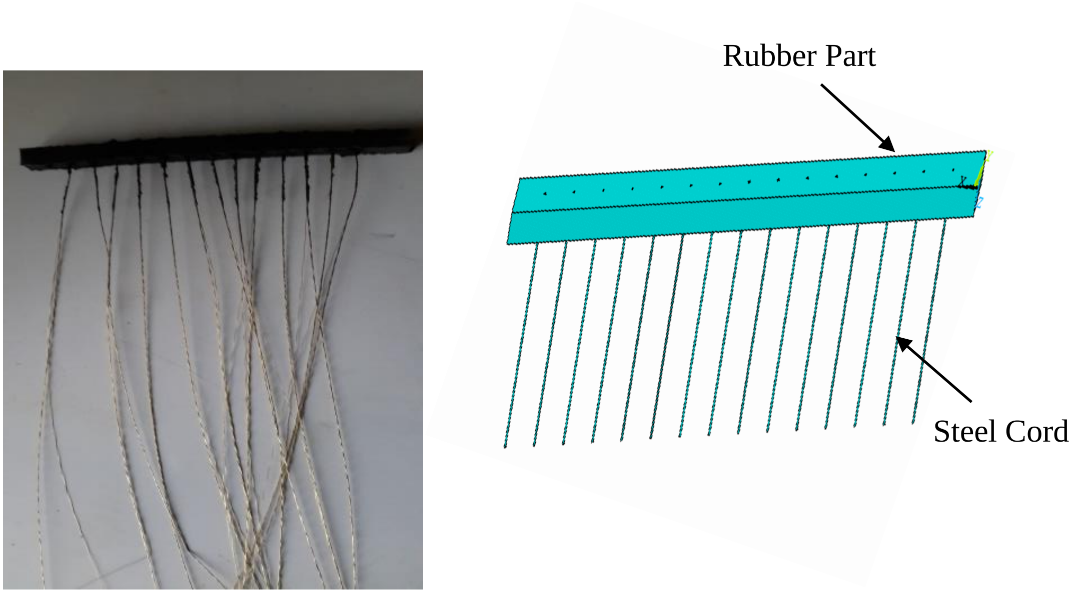

Figure 5: T-Adhesion Specimen After Cleaning.

2.4 Adhesion Test

The vulcanized rubber block with steel cords was released from the mold and left to cool down to room temperature (25 ºC) for a sufficient period of time. This test was carried out in Babylon tires factory according to ASTM D2229.

The device used in this test is Monsanto T10 Tensometer shown in Figure 6 manufactured by Monsanto CO., England. This device is available in Babylon tires factory. The device consists of two shoulder grips which the upper grip used to place the vulcanized rubber block and the free wire is caught in the lower grip. The speed of moving grip is kept at 100mm/min is entered into the controller board of tensometer. When a device is operated, the steel cord pulls out from a block of vulcanized rubber and the result of force was recorded by the printer. Thirty-six samples were tested and then the average force for all wires were taken.

Four samples for any compound were tested at (25, 50, 75 and 100) ºC, the range of temperature was selected according to**(Jamshidi *et.al.*, 2005)**. The average of the pull-out force results were taken.

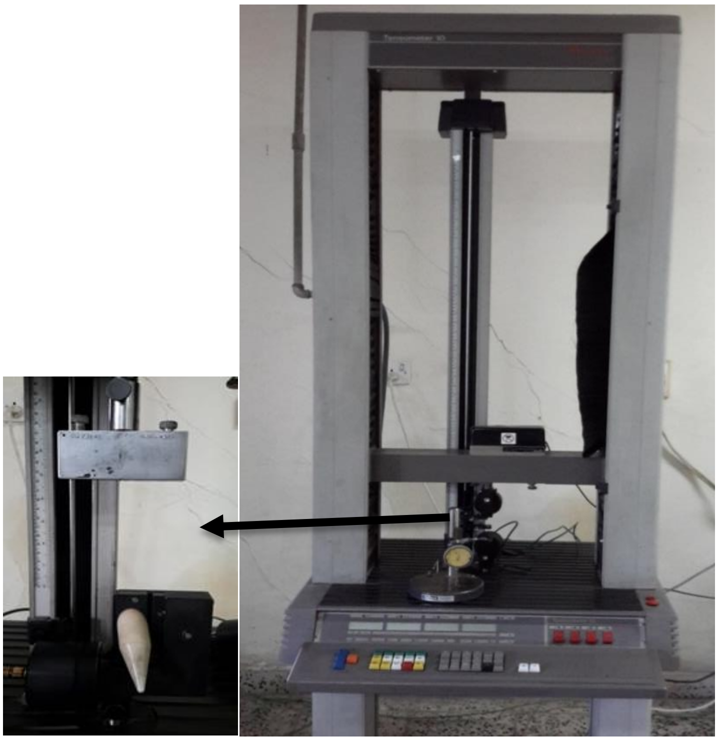

Figure 6: Monsanto T10 Tensometer.

3. Results And Disscusion

The effect of temperature and nano-ZnO on adhesion are studied. Table 3 summarizes the values of T-pull test to get average force in all cords at (25,50,75 and 100) °C temperatures. The results of (A) compound are presented in Figure 7. When the temperature increases, the adhesion decreases due to a destructive effect of hot environment on the interfacial interactions of the system. The increased temperature is the main reason of bond breakage at the interface and re-bonding happens when temperature decreases(**Jamshidi *et.al.*, 2005)**.

Table 3: Pull-out Force Values at Different Temperature of Compounds.

Temperature (°C)		Pull-out Force (N)			
		25	50	75	100
Compound Sample	A	280.64	221.072	213.04	202.8
	B1	142.856	126.7	102.32	76.736
	B2	185.063	166.857	154.78	130.725
	B3	231.59	211.978	190.56	170.6
	B4	250.66	219.75	204.01	200.36
	B5	265.26	221.21	217.056	211.25
	B6	297.72	259.5	237.32	233.311
	B7	215.756	203.91	198.23	187.267
	B8	210.37	192.7	189.204	175.581

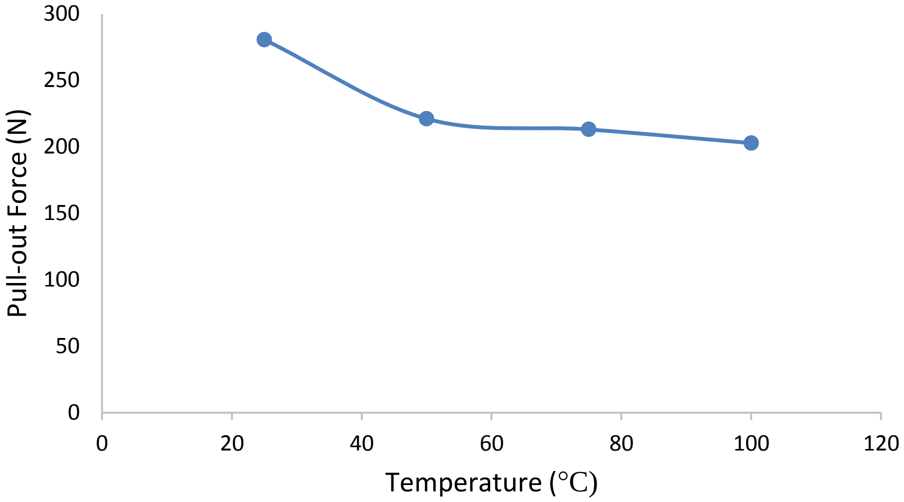

Figure 7: Pull-Out Force of (A) Compound at Different Temperatures.

All aging processes lead to the decrease of the amount of S at the interface CuS. Furthermore, increasing the amount of ZnO and ZnS increases the degradation of adhesion. The ZnO is one factor for degradation due to the zinc ions which leads to degrade rubber crosslink and breaking sulphur ring. In order to reduce this factor, conventional ZnO is replaced by nano-ZnO in rubber compound because the nano-ZnO has a smaller particle size and large surface area than those of conventional ZnO.

The results of the T-pull test which represent the average force in all cords in (B) compounds are summarized in Table 3 and graphed in Figure 8. It is obvious that the increase in a nano-ZnO leads to increase the pull-out force. But a low loading of nano-ZnO is not effective for adhesion due to the efficiency of cross-linking system. This efficiency decreases according to the role of ZnO activator in rubber vulcanization **Roy et al., [2014]**. However, loading with 2.2 pphr of nano-ZnO at (B6) compound has optimum pull-out force then starts to decrease with loading higher than 2.2 pphr. This is attributed to the fact that the increase in the amount of ZnO leads to the increase the Zn^{2+} ions and these ions degrade the adhesion interface. It can also be seen that an increase in temperature causes a decrease the adhesion in all cases.

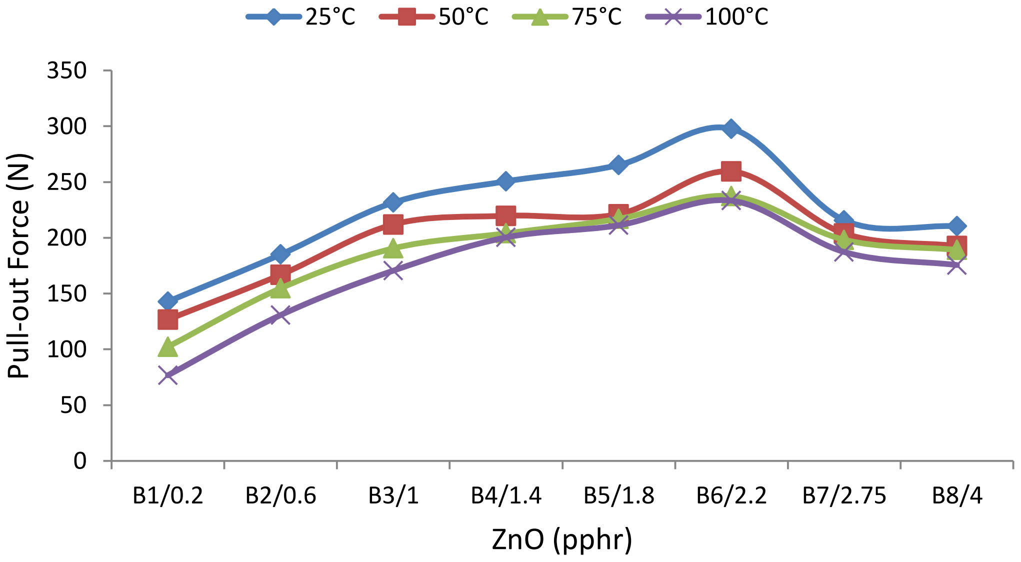

Figure 8: Pull-Out Force of (B) Compounds at Different Temperatures.

To show the effect of nano-ZnO on adhesion, the comparison between B6 (is best compound in group (B) and (A) compound is made. The result of this comparison is that the pull-out force in (B6) compound is greater than that in (A) compound in all the range of temperature shown in Figure 9 this result is because the Zn^{2+} ions in (B6) compound are less than those in the (A) compound. This fact leads to decrease degradation at interface and improving pull-out force by 12%.

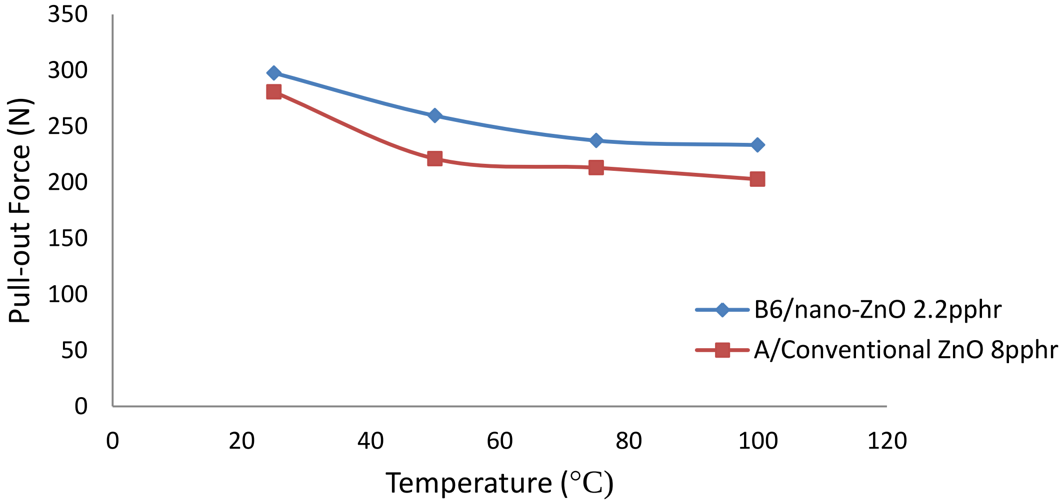

Figure 9: Pull-Out Force of (B6) Compound and (A) Compound at Different Temperatures.

4. Conclusions

This study comes up with following conclusions:

1. Nano-ZnO gives the SMR20 compound optimum pull-out force in all test temperature at 2.2 pphr.
2. Pull-out force with nano-ZnO at 2.2 phr is greater than that of the conventional ZnO at 8 pphr by about of 12%.
3. In all cord-rubber systems an increase in the test temperature causes a decrease in pull-out force.
4. Reduction the amount of ZnO by 72.5%. This reduction is preferable due the fact that ZnO is harmful to the environments.
5. Reduce the cost of compounds due to the price of nano-zinc oxide is approximately equal to the price of conventional zinc oxide.

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